

Studying the effect of thermal and acid exposure on alkali activated slag Geopolymer

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Abstract. This article reports a study about thermal stability as well as acid resistance of geopolymer materials prepared from Ground Granulated Blast Furnace Slag (GGBFS), Air Cooled Slag (ACS), Silica fume (SF) and cement kiln dust (CKD) using 6% (weight) of equal mix from alkaline sodium hydroxide and sodium silicate activators. Study of addition of ACS, SF and CKD as partial replacement of GGBFS is investigated so as to improve the mechanical and microstructural properties of geopolymer mixes. Compressive strength and SEM were utilized in these studies. Materials were prepared using water/binder of 0.30 at 38°C and 100% RH. Results showed that geopolymer materials prepared using alkali activated slag exhibit large changes in compressive strength with increasing the firing temperature from 300 to 1000°C and exhibit an enhancement in thermal stability as compared to concrete specimens. Materials prepared by replacing GGBFS by 15% ACS resist thermal deterioration up to 1000°C. It was suggested to be suitable for refractory insulation applications as well as for production of nuclear concrete reactors. On the other hand, geopolymer mixes exhibit low stability upon subjecting to different concentration from the mix of nitric and hydrochloric acid in equal ratio (1:1). Current studies of geopolymer microstructure were focused on the morphology as well as the relationship between compositions and mechanical properties.

Keywords: Environment, Materials processing, Microstructure, thermal, acid

1. Introduction

Recently discovered geopolymers that are produced by alkaline activation of aluminosilicate raw materials, which are transformed into reaction products by polymerization in a high pH-environment and hydrothermal conditions at relatively low temperatures (up to 120°C). This binder has a great potential as an environmentally favourable alternative to Portland cement. It can produce binder with advantages of Portland cement with a lower cost and a large reduction in CO₂ emissions using industrial waste materials. Examples of this binder type include Class F fly ash (low calcium fly ash) based geopolymer (FFG) [Palomo, et al. (1999), Khale and Chaudhary (2007), Duxson et al. (2007)], and alkali-activated slag cement (AAS) [Song and Jennings (1999)]. Because of low production energy requirements from common raw materials and their inflammability at high temperatures, these compounds attract increasing interest as environmentally friendly, fire proof

building materials, materials for encapsulating hazardous wastes for storage or disposal and also used as sound as well as heat insulators [Davidovits et al., (1994), Lyon et al. (1996)].

GGBS has been used in composite cements and as a cementitious component of concrete for many years and it can be expected that prolonged uses of GGBS will continue for the foreseeable future. On the other hand alkali-activated slag cements using granulated blast-furnace slags were invented by Glukhovsky (1980) and patented in 1958. Alkali activated slags have been employed on a limited scale as oil well cements and as a roof support system in mine applications in South Africa and Canada. Industrial experience of precast products utilizing these cements is widespread in Eastern Europe, Finland and France [Talling and Brandstetr (1989)]. The use of slag as supplementary cementitious material improves concrete durability as it reduces the permeability of GGBS concrete and significantly inhibits the ingress of sulfates [Osborne (1991)]. The

reduction in chloride penetration achieved by GGBS has been confirmed by many different investigators [Pal et al. (2002)]. CKD on the other hand with its fine-grained and high alkali content can be considered as an excellent activator for pozzolanic materials. The dissolution rate of materials with latent pozzolanic properties such as blast furnace slag generally depends on the alkali concentration of the reacting system [Wang, et al. (1995)].

Previous investigations by Davidovits et al. (1994), Barbosa and MacKenzie (2003) reported very good heat resistant properties of materials prepared using sodium silicate, potassium silicate and metakaolin, having thermal stability up to 1200–1400°C. Krivenko and Kovalchuk (2002) investigated heat resistant of geopolymer materials manufactured using class F fly ash, which had good thermal resistance properties up to 800°C. Geopolymers prepared using aluminosilicate materials (fly ash, slag, metakaolin, etc.) have framework structures originating from condensation of tetrahedral aluminosilicate units of varying Al/Si ratio such as $(Al-O-Si-O)^{M+}$, $(Al-O-Si-O-Si-O)^{M+}$, $(Si-O-Al-O-Si-O-Si-O)^{M+}$ etc. M^+ is an alkali ion, typically Na or K, which balances the charge of the tetrahedral Al [Davidovits (1994a)].

Geopolymer cement is also acid-resistant, because unlike the Portland cement, geopolymer cement does not rely on lime and not dissolved by acidic solutions. As shown by the tests of exposing the specimens to 5% of sulfuric acid and chloric acid, geopolymer cements were relatively stable with the weight loss in the range of 5-8%; while the Portland based cements were destroyed and the calcium alumina cement lost weight about 30-60% [Davidovits (1994b)]. Some published papers [Bakharev (2005), Gourley and Johnson (2005), Song et al. (2005)] also reported results of the tests on acid resistance of geopolymers and geopolymer concrete. By observing the weight loss after acid exposure, these researchers concluded that geopolymers or geopolymer concrete is superior to Portland cement concrete in terms of acid resistance as the weight loss is much lower. Bakharev et al. (2003) has also observed that there is a degradation in the compressive strength of test specimens after acid exposure and the rate of degradation depended on the period of exposure. Glukhovskiy (1980) showed that the strength of AAS mortars increased after 1 year in 1–2% $MgSO_4$ solution and stayed constant for 2 years in dilute acids, HCl and H_2SO_4 , while OPC samples deteriorated in six months. Douglas et al. (1992) reported AAS concrete having good resistance to chloride ion penetration with ion penetration ranging from 1311 to 2547 C for 28 days curing and from 676 to 1831 C at 91 days.

The objective of the current study is to investigate the effect partial substitution of GGBFS by ACS, SF and CKD and estimate their stability upon firing at different temperatures from 300–1000°C for 2hrs with a heating rate of 5°C/min by mapping examination using SEM and measuring their compressive strength with temperature change. Also, study the impact of equal mix of nitric and hydrochloric acids at different concentrations (2, 4 and 6molars) on geopolymer behaviour and compare their stability with normal concrete specimens that prepared at the same experimental condition. Also, elucidate the optimum geopolymer mix from water cooled slag, air cooled slag, SF and cement dust upon fire and acid conditions, while focusing on the morphology as well as its relationship between compositions and mechanical properties.

2. Experimental procedures

2.1. Materials

Materials used in this investigation are water cooled slag (known as ground granulate blast furnace slag (GGBFS)) as well as air cooled slag (ACS) sourced from Iron and Steel Factory-Helwan, Egypt. Silica fume from Suez cement company (Helwan plant). Cement kiln by-pass dust (CKD) from Beni-Suef Cement Factory, Egypt.

Two different alkali activators are used sodium silicate solution and sodium hydroxide. Sodium hydroxide (NaOH) brought from SHIDO Company with purity of 99% and liquid sodium silicate (LSS) purchased from Fisher Company consists of 32% SiO_2 and 17% Na_2O with Silica modulus SiO_2/Na_2O equal 1.88 and density 1.46 g/cm^3 ($Na_2SiO_3 \cdot 9H_2O$). Analytic grade concentrated nitric and hydrochloric acid for acid resistance testing in order to prepare 2, 4 and 6 molars in an equal ratio.

Ordinary Portland cement from Helwan Company, Egypt, fine sand (< 1.0 mm) from Oases (Wahat)-Road, Egypt and coarse aggregate composites with a maximum aggregate size of 14 mm for concrete formation as a way of comparison with the produced geopolymer composite. Chemical composition of the starting raw materials was illustrated in Table (1).

Table (1): Chemical composition of starting materials (Mass, %)

Chemical content (%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	TiO ₂	MnO ₂	P ₂ O ₅	Cl	L.O.I.	Total	Moist
Water-Cooled Slag (GGBFS)	36.95	10.01	1.68	33.07	4.43	3.52	0.74	1.30	0.22	3.44	0.100	0.050	0.00	97.69	100-0.00
Air-Cooled Slag (ACS)	31.81	10.35	1.56	34.06	3.05	2.41	0.37	2.15	0.34	4.34	0.005	0.002	0.00	100.00	100-0.34
Ordinary Portland Cement	71.92	4.62	3.39	64.43	1.52	1.14	0.06	0.11	-	-	-	0.050	2.20	100.00	-
By-Prod Cement Kiln Dust (CKD)	0.20	2.04	2.07	51.90	4.57	2.00	3.42	2.63	0.14	0.13	0.13	6.120	19.59	99.90	Free H ₂ O = 15.54
Water (H ₂ O)	95.34	0.05	1.25	0.74	0.16	0.00	0.12	0.28	0.04	0.01	0.02	0.020	1.01	99.78	-

Mineralogical composition of starting raw materials are shown in Figure (1), and illustrating the amorphous structure GGBFS, while ACS is completely crystalline. On the other hand CKD composed mainly of calcite (CaCO₃), sylvite (KCl) and halite (NaCl) in a decreasing order.

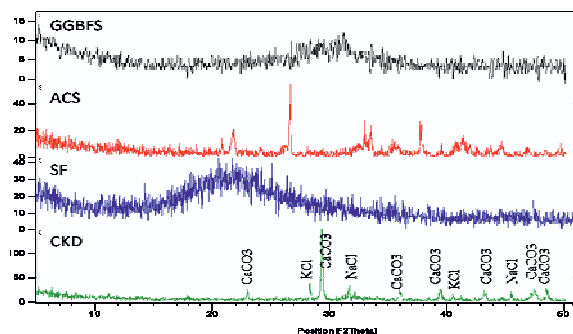


Fig.(1): Mineralogical composition of starting raw materials.

2.2. Geopolymerization and curing

Geopolymers were made by hand-mixing raw materials of each mixture passing a sieve of 90 μm as represented in Table (2) with the alkaline solution for 10 min and a further 5 min using mixer. All investigations involved using of Na₂SiO₃ and NaOH in the ratio of 3:3wt. % of dry mixes, respectively, except mix that contains cement dust; this ratio was chosen based on previous investigations [El-Sayed et al. (2011), Abd.El-Aziz (2010)]. Water-binder ratio (w/b) was 0.30 by mass. Paste mixtures were cast into 25 × 25 × 25 mm cubic-shaped moulds vibrated for compaction and sealed with a lid to minimize any loss of evaporable water. On the other hand, concrete mix was performed using coarse aggregate, fine aggregate and cement in the ratio of 4:2:1, respectively, using water content of 0.30 for better comparison with geopolymer mixes.

Table 2: Composition of the geopolymer mixes.(Mass,%)

Mix no.	Water cooled slag(WCS)	Air cooled slag(ACS)	Silica fume (SF)	Cement kiln dust (ckd)
1	90	—	10	—
2	85	15	—	—
3	75	25	—	—
4	25	50	—	25

All mixes were left to cure undisturbed under ambient temperature for 24 hours, and then subjected to curing temperature of 38°C under 100% relative humidity (R.H.). At the end of the curing regime, the specimens were subjected to compressive strength

measurements and then the resulted crushed specimens were subjected to stopping of the hydration process using stopping solution of alcohol/acetone (1:1) followed by washing with acetone as recommended by different investigators [Saikia et al. (2004)]; to prevent further hydration and for further analysis followed by drying of crushed specimens for 24 hours at 80°C, and then preserved in a well tight container until time of testing. Concrete specimens were prepared as a way of comparison under the same condition using coarse aggregate (14mm): sand (<1.0 mm): cement in the ratio of 4:2:1, respectively.

Firing resistant measurement was done by curing at 38°C and 100%R.H. for 28 days. The samples were calcined at different temperatures (300-1000°C) for 2 hours with a heating rate of 5°C/min [Wenyng et al., (2008)]. Acid-resistant performance: samples were cured in 38°C for 7 days. After that the samples were soaked in a solution of hydrochloric acid and nitric acid in an equal ratio using a concentrations of 2 & 4 and 6 molars up to testing time while acid solution will changed periodically every month so as to retain concentration constant as possible [Wenyng et al., (2008)].

2.3. Methods of investigation

Chemical analysis was carried out using Axios, WD-XRF Sequential Spectrometer (Panalytical, Netherland, 2009) The X-ray diffraction (XRD) analysis was carried out using a Philips PW 1050/70 diffractometer; the data were identified according to the XRD software (pdf-2 database on CD Release 2005). Compressive strength tests were carried out using five tones German Brűf pressing machine with a loading rate of 100 kg/min determined according to ASTM-C109 (2007). Microstructure of the hardened alkali activated slag geopolymer was studied using SEM Inspect S (FEI Company, Netherland) equipped with an energy dispersive X-ray analyzer (EDX). The removal of free water was accomplished by using alcohol/acetone method as recommended by different investigators [Saikia et al. (2004)].

3. Results and discussions

3.1. Fire resistance of slag geopolymer

Scanning electron microscope of alkali activated GGBFS mix specimens that is partially replaced by 10%SF, fired at different firing temperatures are shown in Fig.(2). Morphology of fire untreated specimen (Fig.2a) exhibits a pronounced homogeneous microstructure giving an indication about dissolving most of aluminosilicate materials forming monomer, oligomer and polymeric three dimensional structure network forming an

amorphous geopolymer composition. It is also noticed the coexistence of hydration materials (CSH) with geopolymer network forming a tough and well compacted structure which will be positively reflected on the mechanical strength of this mixture. Heating at 500°C, SF-specimen did not experience large change in its topography in spite of a slight densification; also there are a great contributions as well as transformation of reacted materials into crystalline reaction products (Fig.2b). A significant increase in the matrix porosity was observed after firing at 800°C with the presence of wide gaps within the reaction products (Fig.2c), as explained by low matrix cohesion up on high firing temperature which resulted from dehydroxylation of geopolymer network that in turn lead to weakness of its mechanical properties. After firing at 1000°C, area of low porosity and large pores dominated the matrix (Fig.2d). Development of these large pores is possibly connected to the material decomposition upon heating as well as dehydroxylation of geopolymer composite.

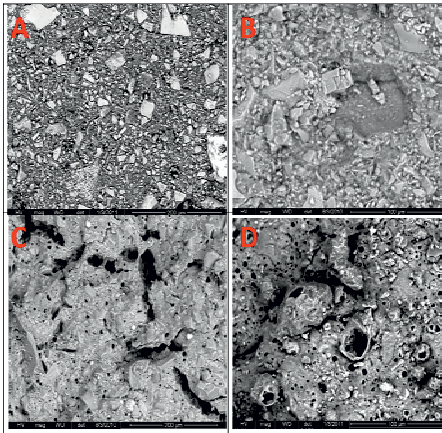


Fig.(2): SEM micrograph of alkali activated specimens using 3:3 sodium hydroxide to sodium silicate having 10%SF and 90%WCS (a) unfired sample, (b) fired at 500°C, (c) fired at 800°C and (d) fired at 1000°C.

Figure 3, depicts the morphology and microstructure of various geopolymer compositions fired at 800 and 1000°C for 2 hours with a heating rate of 5°C/min. Morphology of SF-geopolymer matrix fired at 800°C reflects loose compaction between the geopolymeric matrix and hydration materials resulting from dehydroxylation of geopolymer structure (Fig.3a), whilst the morphology of 15 % ACS and 85 % GGBFS mix specimen implements better geopolymer matrix stability upon firing at 800°C with the presence of high geopolymer contribution area, whereas a traceable amount of efflorescence of sodium carbonate spreaded on matrix surface (Fig.3b). Figure (3c), shows the

morphology of 25 % ACS geopolymer mix as partial replacement of water cooled slag constituent, where thermal stability decreased up on increasing of air cooled slag, as the higher crystalline content leads to the decrease in amorphous GGBFS content with the increase of air cooled slag.

Increasing firing temperature up to 1000°C leads to development of large pores that possibly connected to material decomposition upon heating which accompanied by the increase of average pore size in SF geopolymer mix (Fig.3d), this is will possess a pessimism effect on the matrix stability and hence its mechanical characteristics. Using 15 %ACS (Fig.3e) gives better microstructure characteristics as compared with SF-geopolymer mix. The replacement of GGBFS by 15 %ACS leads to the formation of geopolymer structure that can withstand even at this high temperature and possess a thermal stability higher than that of comparable SF-mix of geopolymer mix contains; this thermal stability can be related to the better rearrangement of geopolymer structure by partial replacement of GGBFS by ACS that results in a formation of compact matrix, where ACS grains are much harder than GGBFS grains if replaced in a lower dose [Heikal et al., (2004)], so this replacement will positively enhance the mechanical and microstructural characteristics upon using 15 % ACS.

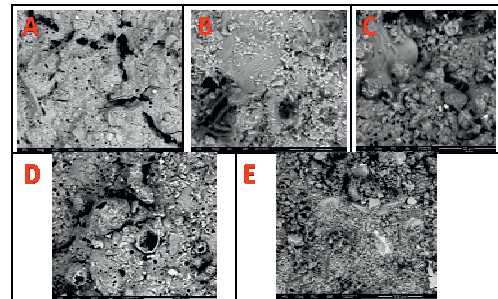


Fig.(3): SEM micrograph of alkali activated specimens using 3:3 sodium hydroxide to sodium silicate (A) 10%SF and 90%WCS fired at 800°C, (B) 85%WCS and 15%ACS fired at 800°C, (C) 75%WCS and 25%ACS fired at 800°C, (D) 10%SF and 90%WCS fired at 1000°C, and (E) 85%WCS and 15%ACS fired at 1000°C.

The term fire resistance is frequently used to assess the behaviour after firing of different samples as indicated from (Fig. 4), illustrating strength pattern of geopolymer specimens prepared using 3:3 sodium hydroxides to sodium silicate activator and indicate thermal stability of the geopolymer mixes to firing treatment up to 500°C except for mix contains 25 % CKD as compared with concrete specimens prepared and treated at the same conditions. This thermal stability was coincided with previous findings stated that beyond 300°C, no shrinkage or expansions were recorded until 700°C. Between 700°C and 800°C,

further increase in shrinkage was observed. Shrinkage occurred due to mass loss in geopolymer when subjected to elevated temperature [Kong and Sanjayan (2008)].

The figure also illustrates thermal stability of SF-mix up to 500°C followed by a steep decrease up to 800°C which may be connected to a dramatic increase of the average pore size as the amorphous structures were replaced by the crystalline Na-feldspars; that in turn contributed to increase in porosity and strength deterioration [Bakharev (2006)]. This suggests that dehydration causes contraction of the gel resulting in aggregation of pores that can be observed by SEM, (Fig. 2c, d).

Geopolymer mix of 15% air cooled slag (ACS) exhibits a pronounced withstand to high fire temperature as compared with other mixes up to 1000°C and did not exhibit a thermal deterioration as reflected from its morphology (Fig.3b,e). This may be due to the partial replacement of GGBFS by ACS results in a formation of compact matrix, as ACS grains are much harder than GGBFS grains if replaced in a lower dose [Heikal (2004)]. Continuous increase in ACS up to 25% results in thermal deterioration beyond 800°C (Fig.3c), which explained by the increase of crystalline content on the expense of amorphous geopolymer content leading to decrease in thermal stability of the reaction products. It is known that strength and microstructure stability after firing is an indication of good fire resistance in refractory context. While fire resistance in a fire-protection context is based upon heat conduction through a sample when exposed to standard fire defined by Wickström and Hadziselimovic (1996).

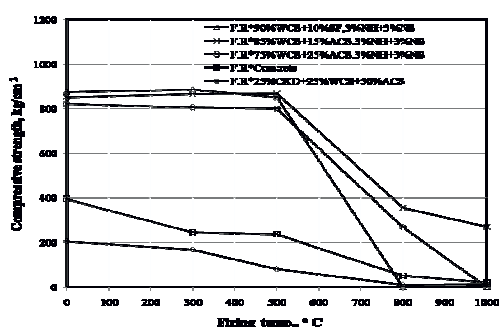


Fig.(4): Compressive strength of fired alkali activated geopolymer specimens at different firing temperatures (using 3:3 sodium hydroxide to sodium silicate).

Adding 25%CKD along with both air and water-cooled slag (GGBFS) implement a lower thermal stability as compared with all other geopolymer mixes and even with concrete specimen. It is possible due to rapid deterioration of materials prepared using CKD due to lower reaction degree of CKD,

incomplete polymerization of geopolymers and because of impurities present in the dust that lowered the melting temperature of these materials [Van Vlack (1964)]. Excess alkalis in CKD especially sodium in addition to the added Na-containing activators have high diffusion coefficient on firing thus lower thermal stability of the matrix. Concrete specimen has lower thermal stability as the geopolymeric cement concrete was superior to Portland cement in terms of heat and fire resistance, where the Portland cement experienced a rapid deterioration in compressive strength at 300°C, whereas the geopolymeric cement specimens were stable up to 600°C as recorded by Davidovits et al., (1994).

3.2. Acid resistance of geopolymer mixes

Figure (5) elucidates the visual appearance of geopolymer specimens after soaking in an equimolar ratio of HCl and HNO₃ at a concentration of four molar up to 4 months as compared with concrete mix prepared at the same condition. It can be seen that the SF-geopolymer specimen (Fig.5a) exposed to 4 molars mix of acids undergoes etches at the corner of the cubes and it can be noticed also that this geopolymer mix possess little damage as compared with other specimens, while at later ages suffers from complete deterioration. Geopolymer mix that has 25 % ACS (Fig.5b) exposed to surface as well as edges erosion of the cubic specimen. The severity of the damage and distortion of the specimen's shape depended on the concentration of the solution. Where, the mix that has 25 % CKD shows a gelatinous structure reflecting the rapid deterioration and its weak acid resistance (Fig.5d). Concrete specimen on the other hand exhibits deterioration from all sides as well as from the interior of the cubic specimen (Fig.5c), as coincide with low resistivity of concrete structure to acid medium.

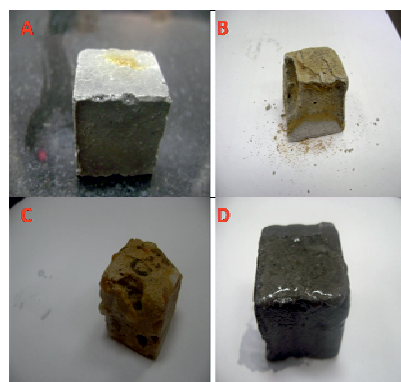


Fig. (5): Visual appearance of geopolymer specimens after 4 months exposed to 4 molars acid solution of HCl:HNO₃ in an equimolar ratio (a)10%SF and 90%WCS,(b)75%WCS+25%ACS,(c)concrete, and(d) 25%CKD+25%WCS and 50%ACS

Figures (6, 7) represent compressive strength of the studied geopolymer mixes as well as concrete specimens that exposed to 2, 4 and 6 molar acid solutions, but the patterns of acid resistance are empty from the higher concentration (6M) as all specimens suffers from complete deterioration at the last mentioned concentration. Strength of all mixes decrease with acid concentration increase as well as with curing age. Increase of acid solution higher than 4 mol/L, leads to a complete deterioration and dissolution of geopolymer mixes. It is known that reaction product of geopolymer is a kind of three-dimensional structure in which the tetrahedral SiO_4 and AlO_4 units are polycondensed with the alkaline ions balancing the charge [Davidovits (1997)]. It is mainly the amorphous analogue of zeolite and feldspar. Although most of alkalis are fixed into the three-dimensional structure, some alkali can remain in soluble form. This free alkali is easily dissolved, which generates an increase in the porosity of the specimen and consequently a decrease in its strength [Alomo et al. (1999)].

Visual examination confirms that SF-mix has higher strength values up to 3 months, while samples suffered from different erosion degrees in different acid solutions as revealed from Figure (5). Increased replacement of GGBFS by 25 % ACS, leads to lowering its resistance as reflected from its strength. The increased content of ACS decreases amorphous geopolymer structure that can be reflected on its acid resistance (Fig.6).

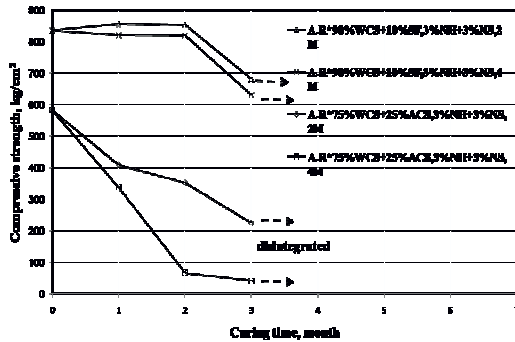


Fig.(6): Compressive strength of geopolymer specimens exposed to 2 and 4 molar acid solution of HCl:HNO₃ in an equimolar ratio.

Uses of 25 % CKD provides an extra alkali to the matrix which in turn leads to increase in the average pore size and porosity [Kong et al. (2008)] and so it will be more susceptible to acid penetration and dissolution providing strength value that lowered than the concrete mix which is known by its weak acid resistance (Fig.7). When the pH value of acid solution decreases, the geopolymer medium will be disturbed and favor the oligomer dissolution than

geopolymer formation and precipitation formation. Also, the free alkalis can balance the H⁺; the compressive strength will not decrease [Wenyang et al. (2008)], but when the concentration of H⁺ is higher, many free alkalis react with the H⁺ and causes strength decrease.

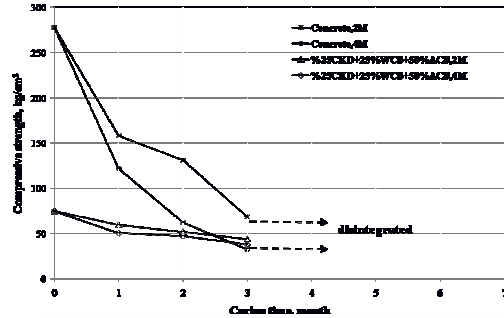


Fig.(7): Compressive strength of geopolymer specimens exposed to 2 and 4 molar acid solution of HCl:HNO₃ in an equimolar ratio

4. Conclusion

- 1- The geopolymer materials prepared with sodium-containing activators exhibit thermal stability up to 500°C more than that obtained by normal concrete mix specially those contains SF and ACS which could be used in the manufacture of nuclear power plant.
- 2- Partial substitution of GGBFS by 15% ACS possesses a thermal stability up to 1000°C reflecting the amorphous geopolymer behavior which resists heat treatment and can be used in the refractory bricks. Increasing ACS content to 25% lowers the thermal stability of geopolymer composition.
- 3- Partial substitution of GGBFS by 10% SF with its amorphous structure exhibit thermal stability up to 500°C giving strength values that exceed the comparable ACS mixes, but strength diminishes beyond this temperature while ACS mixes resist deterioration up to 800°C.
- 4- Most geopolymer mixes as well as concrete specimen have low acid resistance and deteriorated after 3 months of immersion in acids; these were revealed from their loss in strength and were emphasized from the images of the visual examination, where the decreased pH leads to destabilization and dissolution of geopolymer structure.
- 5- Strength of 25% air cooled slag mixes decrease up to complete diminishes beyond 3 months, while SF mixes resist acid deterioration up to 2 months providing strength values exceed that of ACS mixes. On the other hand, mixes have 25%CKD provide lowest stability up on acid immersion as reflected from their strength values which lowered than that of concrete mixes.

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